Thermoelastic Fluctuations in $Solids^1$

 $T.H.K.Barron^{2,3}$ and $A. Padmaja^4$

Paper presented at the Fourteeenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.

² School of Chemistry, University of Bristol, Bristol BS8 1TS, England.

 $^{^{3}}$ To whom correspondence should be addressed.

 $^{^4\,}$ 828, NW Oak, Corvallis, Oregon 97330, U.S.A.

ABTRACT

Adiabatic thermoelastic heating can be used to monitor stress fluctuations in solids. Previous studies of the effects on the temperature fluctuations both of applied static stress and of the finite amplitude of the stress fluctuations have used approximate theory. The present rigorous thermodynamic treatment distinguishes between adiabatic second order derivatives needed for finite amplitude and mixed derivatives needed for static applied stress. A detailed analysis is given for purely compressive stress, followed by computations for KCl, NaCl, Al, Cu, Ti, and the alloy Ti-6Al-4V. Additional terms revealed by the new analysis prove to be substantial, including the difference between the adiabatic and mixed derivatives. Revised forms are then proposed for earlier approximations. For unidirectional stress, expressions are taken from an analysis given elsewhere; and computations made for Al, Cu, Ti and Ti-6Al-4V. Corrections to earlier approximations are relatively smaller than for compressive stress, and of opposite sign because the shear component of the unidirectional stress dominates the second order effects.

1. INTRODUCTION

Oscillating stresses in solids give rise to oscillations in temperature. This provides a means of monitoring stress fluctuations in a material: the associated temperature fluctuations are scanned over the surface of the material with the aid of a sensitive infra-red detector [1].

Although in applications important effects can arise from frictional processes and from heat flow, in essence the phenomenon is adiabatic. It is sometimes characterised by a "thermoelastic constant", defined by [2]

$$K = -\frac{1}{T_0} \left(\frac{\Delta T}{\Delta \sigma} \right)_S,\tag{1}$$

where T_0 is the mean temperature and ΔT is the amplitude of the adiabatic cyclic change in temperature caused by a cyclic change in the sum of the principal stresses of amplitude $\Delta \sigma$. We may note, however, that eq.(1) defines K uniquely only for isotropic or cubic materials under hydrostatic pressure, since otherwise ΔT depends upon the directions of the principal stresses and how $\Delta \sigma$ is distributed among them. Furthermore, even these materials lose their symmetry as soon as an anisotropic stress is applied, and so the derivatives of K with respect to such stresses are ill-defined. We shall therefore retain K only for isotropic or cubic materials under isotropic pressure, and redefine it as the "thermoelastic coefficient"

$$K = (1/3T)(\partial T/\partial P)_S. \tag{2}$$

For anisotropic stresses we shall refer only to the stress derivatives of T.

In any case, to refer to K as a "constant" can be misleading, because a stress derivative of T is itself stress-dependent [3, 4]. This gives rise to two second order

effects: (i) the temperature response to stress fluctuations about a mean stress σ_m varies with σ_m ; (ii) the temperature response to a sinusoidally varying stress includes a second harmonic of double the applied frequency.

Wong et al. [4, 5] developed a method for calculating the magnitude of these effects from other properties of the material. Although they started with time-dependent equations which took account both of heat flow and of internal heat sources, they discarded all such non-equilibrium processes before reaching their result, which was thus purely thermodynamic. They tested the method experimentally for unidirectional stress fluctuations in the titanium alloy Ti-6Al-4V, obtaining good agreement with experiment [5]. However, their theory employed a number of approximations in the thermodynamics which were not discussed or assessed; in particular, the distinction between adiabatic and isothermal second derivatives was largely ignored.

Subsequently Ledbetter et al. [6] considered the effect of pressure rather than unidirectional stress. They used three different expressions for the pressure dependence of K: one was derived by rough approximations from a Mie-Grüneisen pair potential, another from the theory of Wong et al., and the third from the second by further approximations due to Chang [7] which are not always reliable [8]. These expressions gave values which agreed with each other in order of magnitude for each of eight metals studied, differing by 20 to 50%.

In the present paper we derive exact thermodynamic expressions for the temperature response of a material subjected to oscillating stress or pressure. We investigate for various materials the importance of terms neglected in the approximations of Wong et al. and Ledbetter et al. In §2 we point out that it is the isothermal stress derivative

of $(\partial T/\partial \sigma)_S$ which determines the effect of the mean stress σ_m , and the adiabatic stress derivative which determines the amplitude of the second harmonic response. In §3 rigorous thermodynamic expressions are derived for the pressure effects, and the approximations of Ledbetter *et al.* are modified accordingly. Calculations on various materials show that additional terms neglected in the method of Wong *et al.* make substantial contributions. In §4 expressions for unidirectional stress are quoted from a more general analysis for orthorhombic symmetry given elsewhere [9]. Calculations show that corrections to the theory of Wong *et al.* are still appreciable, but much less important than for purely compressional stress.

2. THE STEADY-STATE RESPONSE TO FLUCTUATING STRESS

Wong et al. [5] applied their theory to a unidirectional stress, denoted here by σ_U , with both static and sinusoidal components:

$$\sigma_U = \sigma_m + \Delta\sigma\sin\omega t,\tag{3}$$

where σ_m and $\Delta\sigma$ are constants. We start by taking the more general form

$$\sigma_U = \sigma_m + \sigma_v, \tag{4}$$

where σ_m is the mean stress and σ_v is an oscillating component of arbitrary shape, so that

$$\langle \sigma_U \rangle = \sigma_m, \quad \langle \sigma_v \rangle = 0,$$
 (5)

where $\langle \cdots \rangle$ denotes averaging over a long time. In an ideal non-lossy material, the mean temperature will relax over a sufficiently long time to the ambient temperature T_0 . The steady-state response is thus purely oscillatory, and is determined by $(\partial T/\partial \sigma_U)_S$,

which is itself stress-dependent. Moreover, the effects of σ_m and σ_v on $(\partial T/\partial \sigma_v)_S$ must be considered separately. In the steady-state, σ_m has no effect upon the temperature, so that its effect on $(\partial T/\partial \sigma_v)_S$ is isothermal; whereas in the limit of rapid oscillations the effect of σ_v is adiabatic. To the first order in the stress, therefore,

$$\left(\frac{\partial T}{\partial \sigma_U}\right)_S = \left(\frac{\partial T}{\partial \sigma_U}\right)_{S;0} + \left[\frac{\partial}{\partial \sigma_U}\left(\frac{\partial T}{\partial \sigma_U}\right)_S\right]_{T;0} \sigma_m + \left[\frac{\partial^2 T}{\partial \sigma_U^2}\right]_{S;0} \sigma_v, \tag{6}$$

where the subscript 0 denotes evaluation at $\sigma_U = 0$, $T = T_0$. Integration with respect to σ_v then gives

$$T - T_0 = \left\{ \left(\frac{\partial T}{\partial \sigma_U} \right)_{S;0} + \left[\frac{\partial}{\partial \sigma_U} \left(\frac{\partial T}{\partial \sigma_U} \right)_S \right]_{T;0} \sigma_m \right\} \sigma_v + \frac{1}{2} \left[\frac{\partial^2 T}{\partial \sigma_U^2} \right]_{S;0} \left\{ (\sigma_v)^2 - \langle (\sigma_v)^2 \rangle \right\}, (7)$$

where the constant term is fixed by the steady-state condition $\langle T \rangle = T_0$.

For the sinusoidal oscillation $\sigma_v = \Delta \sigma \sin \omega t$, this becomes

$$T - T_0 = \left\{ \left(\frac{\partial T}{\partial \sigma_U} \right)_{S;0} + \left[\frac{\partial}{\partial \sigma_U} \left(\frac{\partial T}{\partial \sigma_U} \right)_S \right]_{T;0} \sigma_m \right\} \Delta \sigma \sin \omega t - \frac{1}{4} \left[\frac{\partial^2 T}{\partial \sigma_U^2} \right]_{S;0} (\Delta \sigma)^2 \cos 2\omega t.$$
(8)

The response to an applied pressure $P=P_m+\Delta P\sin\omega t$ is similarly

$$T - T_0 = \left\{ \left(\frac{\partial T}{\partial P} \right)_{S;0} + \left[\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P} \right)_S \right]_{T;0} P_m \right\} \Delta P \sin \omega t - \frac{1}{4} \left[\frac{\partial^2 T}{\partial P^2} \right]_{S;0} (\Delta P)^2 \cos 2\omega t. \tag{9}$$

In eqs.(8-9) the small second order terms in $\cos 2\omega t$ do not alter the amplitude ΔT of the cyclic change in T, since they raise the maximum and minimum temperatures by the same amount. To this approximation, therefore, the thermoelastic "constant" of eq.(1) is independent of the amplitude of the fluctuations; and its dependence on the mean stress is given by a mixed isothermal/adiabatic derivative of T. On the other hand, the magnitude of the second harmonic response depends on the square

of the amplitude $(\Delta \sigma)^2$ or $(\Delta P)^2$ as given by the purely adiabatic second derivative $[\partial^2 T/\partial \sigma_U^2]_S$ or $[\partial^2 T/\partial P^2]_S$.

The result of Wong *et al.* [5] for unidirectional stress is given by their eq.(2.6), which may be written in the present notation as

$$\frac{C_{\eta}}{V} \left(\frac{T - T_0}{T_0} \right) = -\left(\alpha - \frac{1}{E^2} \frac{\partial E}{\partial T} \sigma_m \right) \Delta \sigma \sin \omega t - \frac{1}{4E^2} \frac{\partial E}{\partial T} (\Delta \sigma)^2 \cos 2\omega t, \tag{10}$$

where C_{η} is the heat capacity at constant strain, V is the volume, α is the coefficient of linear expansion in the direction of the stress, and E is Young's modulus (whether E_S or E_T is not specified). Comparison of eq.(10) with eq.(8) shows that Wong *et al.* do not distinguish between the different kinds of second order derivatives. For unidirectional stress their approximations are equivalent to taking

$$\left(\frac{\partial T}{\partial \sigma_U}\right)_{S:0} \approx -\alpha T V / C_{\eta}, \tag{11}$$

and

$$\left[\frac{\partial}{\partial \sigma_{U}} \left(\frac{\partial T}{\partial \sigma_{U}}\right)_{S}\right]_{T:0} \approx \left[\frac{\partial^{2} T}{\partial \sigma_{U}^{2}}\right]_{S:0} \approx -\frac{TV}{C_{\eta}} \left[\frac{\partial}{\partial T} \left(\frac{1}{E}\right)\right]_{\sigma:0}.$$
 (12)

However, such approximations are unnecessary, because exact thermodynamic expressions for the various stress derivatives are obtainable. In the next section the general method is illustrated in detail by its simplest application, viz. to a solid under fluctuating hydrostatic pressure. Unidirectional stress is treated more briefly in §4.

3. TEMPERATURE RESPONSE TO FLUCTUATING PRESSURE

3.1 Thermodynamic Expressions

Experimental quantities from which thermoelastic pressure effects can be derived are the volume V, the adiabatic compressibility χ_S (or bulk modulus B_S)

$$\chi_S = (1/B_S) = -(1/V)(\partial V/\partial P)_S, \tag{13}$$

the coefficient of volumetric expansion β , and the heat capacity at constant pressure C_P , together with their temperature derivatives at constant pressure; alternatively, C_P and V may be replaced by the specific heat per unit mass c_P and the density ρ , since they are needed only in the combination $C_P/V = \rho c_P$. The derivatives in eq.(9) are then obtained from the following thermodynamic analysis.

The Maxwell relation

$$(\partial T/\partial P)_S = (\partial V/\partial S)_P \tag{14}$$

gives immediately

$$\left[\frac{\partial T}{\partial P}\right]_{S} = \left[\frac{\partial V}{\partial T}\right]_{P} \left[\frac{\partial T}{\partial S}\right]_{P} = \frac{\beta V T}{C_{P}} = \gamma \chi_{S} T, \tag{15}$$

where γ is the thermodynamic Grüneisen function defined by (see, e.g., [10, 11])

$$\gamma \equiv \left[\frac{\partial P}{\partial (U/V)} \right]_V = -\left[\frac{\partial \ln T}{\partial \ln V} \right]_S = \frac{\beta V}{\chi_S C_P}. \tag{16}$$

Eqs.(13-14) then give for the adiabatic second pressure derivative

$$\left[\frac{\partial^2 T}{\partial P^2}\right]_S = \frac{\partial^2 V}{\partial P \partial S} = -\left[\frac{\partial}{\partial S}(V\chi_S)\right]_P$$

$$= -\frac{T}{C_P}\left[\frac{\partial}{\partial T}(V\chi_S)\right]_P$$

$$= -\frac{VT}{C_P}\left\{\left[\frac{\partial \chi_S}{\partial T}\right]_P + \beta \chi_S\right\}$$

$$= -(\beta V T \chi_S/C_P)(\delta_S + 1), \tag{18}$$

where δ_S is the adiabatic Anderson-Grüneisen function defined by Basset *et al.* [13]:

$$\delta_S = -\left[\frac{\partial \ln B_S}{\partial \ln V}\right]_P = \left[\frac{\partial \ln \chi_S}{\partial \ln V}\right]_P = -\frac{1}{\beta B_S} \left[\frac{\partial B_S}{\partial T}\right]_P. \tag{19}$$

The isothermal pressure derivative may then be obtained from the identity

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P}\right)_{S}\right]_{T} = \left[\frac{\partial^{2} T}{\partial P^{2}}\right]_{S} - \left[\frac{\partial}{\partial T} \left(\frac{\partial T}{\partial P}\right)_{S}\right]_{P} \left(\frac{\partial T}{\partial P}\right)_{S},\tag{20}$$

which with the aid of eqs.(15) and (17) gives the derivative explicitly in terms of primary experimental quantities:

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P}\right)_{S}\right]_{T} = -\frac{VT}{C_{P}} \left\{ \left[\frac{\partial \chi_{S}}{\partial T}\right]_{P} + \beta \chi_{S} + \frac{V\beta}{C_{P}} \left(\beta + \beta^{2}T + T\left[\frac{\partial \beta}{\partial T}\right]_{P} - \frac{\beta T}{C_{P}} \left[\frac{\partial C_{P}}{\partial T}\right]_{P}\right) \right\}.$$
(21)

In contrast, the method of Wong et al. gives for the second derivatives (cf. eq.12)

$$\left[\frac{\partial^2 T}{\partial P^2}\right]_S \approx \left[\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P}\right)_S\right]_T \approx -\frac{VT}{C_V} \left[\frac{\partial \chi}{\partial T}\right]_P. \tag{22}$$

Eq.(17) shows that it is the adiabatic compressibility whose isobaric temperature derivative is required, that the denominator should be C_P (rather than C_{η} or C_V), and that there is an additional term in $(\partial^2 T/\partial P^2)_S$. Eq.(21) shows that there are further additional terms in $[(\partial/\partial P)(\partial T/\partial P)_S]_T$.

The results obtained in this subsection apply not only to isotropic material but also to any homogeneous material under hydrostatic pressure.

3.2. Pressure Derivative of the Thermoelastic Coefficient

For a cubic or isotropic material, the thermoelastic coefficient of eq.(2) is given by

$$K = \frac{1}{3} \left(\frac{\partial \ln T}{\partial P} \right)_S = \frac{1}{3} \beta V / C_P = \frac{1}{3} \gamma \chi_S.$$
 (23)

Approximate thermodynamic expressions for its pressure derivative have been suggested by Ledbetter $et\ al.^1$:

$$\frac{1}{K_0} \left(\frac{\partial K}{\partial P} \right) \approx -\frac{\delta}{B_0} \approx -\frac{1}{B_0} \left(\frac{dB_T}{dP} - 1 \right) \approx -\frac{1}{B_0} \left(\frac{dB_S}{dP} - 1 \right). \tag{24}$$

Like those of Wong *et al.*, these expressions do not distinguish fully between adiabatic and isothermal processes. We have seen in §2 that it is the mixed second derivative of

¹A correction factor of one third has been applied.

eq.(21) that is relevant to the pressure dependence of K. Using this derivative, and also by direct differentiation of the last of eqs.(23) [12], exact expressions can be obtained in place of those of eqs.(24):

$$\frac{1}{K} \left(\frac{\partial K}{\partial P} \right)_T = -\frac{\delta_S}{B_T} - \frac{1}{B_S} \{ 1 + \gamma + (\partial \gamma / \partial \ln T)_P \}$$
 (25)

$$= -\frac{\delta_T}{B_T} - \frac{1}{B_S} \{ 1 - (VT/C_P)(\partial \beta/\partial T)_P \}$$
 (26)

$$= -\frac{1}{B_S} \left(\left[\frac{\partial B_S}{\partial P} \right]_T + (1 + \beta \gamma T) q \right), \tag{27}$$

where B_T is the isothermal bulk modulus $B_S/(1+\beta\gamma T)$, δ_T is the isothermal Anderson-Grüneisen function $(\partial \ln \chi_T/\partial \ln V)_P$ (see [13]), and

$$q = (\partial \ln \gamma / \partial \ln V)_T = (V/\gamma)(\partial \gamma / \partial V)_T, \tag{28}$$

sometimes called the second Grüneisen function².

At high temperatures $(\partial \beta/\partial T)_P$ and $(\partial \gamma/\partial T)_P$ are usually fairly small, $\beta \gamma T$ and hence the difference between B_S and B_T seldom exceed 10%, and (less reliably) q is often about unity. Eqs.(25-27) thus suggest the following rough approximations as modifications of eqs.(24):

$$\frac{1}{K} \left(\frac{\partial K}{\partial P} \right)_T \approx -\frac{\delta_S + 1 + \gamma}{B_S} \approx -\frac{\delta_T + 1}{B_S} \approx -\frac{(\partial B_S / \partial P)_T + 1}{B_S}.$$
 (29)

3.3. Experimental Magnitudes and Discussion

We have used eqs. (15,17,21) to calculate pressure derivatives of T for several of the materials considered by Wong $et\ al.$ and Ledbetter $et\ al.$, and also for two alkali halides.

²At any point where the thermal expansion changes sign, β , γ and K are zero and δ_S and q infinite. Eq.(18) is then indeterminate, although the equivalent eq.(17) is still valid.

It is difficult to estimate error in the primary data, and different measurements often disagree, especially at room temperature where high and low temperature ranges meet. The values we have adopted are good enough to let us assess the relative importance of different terms in the thermodynamic expressions, but we have not attempted a critical assessment of all available data. We give only the room temperature values (Table I), although for all the materials except the titanium alloy we have calculated pressure derivatives and K over a range of temperatures. Table II lists values for room temperature and one higher and one lower temperature, together with the quantity $W2P = -(VT/C_P)(\partial\chi_S/\partial T)_P$. W2P is the first term in eq.(17), and gives the value obtained by the method of Wong et al., except for the factor C_V/C_P which is close to unity. Table II shows that at all temperatures the mixed derivative is larger than the adiabatic derivative, typically by a factor of about 1.5, although less (about 1.25) for Ti and Ti-6Al-4V. Neither derivative is approximated closely by W2P; the adiabatic and mixed derivatives are greater by factors of about 1.3 and 1.8 respectively.

Table III gives room temperature isothermal pressure derivatives of $\ln K$, compared with the approximations of eqs.(29). The approximations have errors of about 10% or less, except for Al, where the 20% error for the third approximation appears to stem from a high value of q. Similar calculations made at other temperatures showed that K and its isothermal pressure derivative increase fairly slowly with temperature, typically by about 10% every 100 K. The first two approximations of eqs.(29) remained accurate to within about 10%, the first approximation being closest at low temperatures and the second at high temperatures; the third approximation was not tested because the values of $(\partial B_S/\partial P)_T$ were not readily available.

4. RESPONSE TO FLUCTUATING UNIDIRECTIONAL STRESS

4.1. Thermodynamic Expressions

The derivation of expressions for second order stress derivatives is more complex than for pressure derivatives, mainly because there are no finite strain coordinates thermodynamically conjugate to elements of the Cauchy stress tensor $\sigma_{\alpha\beta}$. A rigorous analysis for orthorhombic symmetry is given elsewhere [9], which includes as a special case unidirectional stress σ_U in an isotropic material. This gives

$$\left(\frac{\partial T}{\partial \sigma_U}\right) = -\frac{1}{3} \left(\frac{\partial T}{\partial P}\right) = -\left(\frac{VT}{C_P}\right) \alpha,$$
(30)

$$\left[\frac{\partial^2 T}{\partial \sigma_U^2}\right]_{S:0} = -\left(\frac{VT}{C_P}\right) \left[\left(\frac{\partial (1/E_S)}{\partial T}\right)_P - \alpha \left(\frac{1+4\nu_S}{E_S}\right)\right] \tag{31}$$

$$\left[\frac{\partial}{\partial \sigma_{U}} \left(\frac{\partial T}{\partial \sigma_{U}}\right)_{S}\right]_{T:0} = \left[\frac{\partial^{2} T}{\partial \sigma_{U}^{2}}\right]_{S:0} - \left(\frac{TV^{2} \alpha^{2}}{C_{P}^{2}}\right) \left[1 + \beta T - \left(\frac{\partial \ln C_{P}}{\partial \ln T}\right)_{P} + \left(\frac{\partial \ln \beta}{\partial \ln T}\right)_{P}\right] (32)$$

where E_S and ν_S are respectively the adiabatic Young's modulus and Poisson's ratio. Comparing these with Wong's approximations of eqs.(11-12), we see that C_{η} should be replaced by C_P , that the Young's modulus required is E_S , and that there are additional terms in the second derivatives which then differ from each other.

4.2. Experimental Magnitudes and Discussion

We have used eqs.(31-32) to compute second order unidirectional stress derivatives of T for some metals, including the alloy studied by Wong et al. [5]. Table IV gives some results, together with E_S and its temperature derivative (other data is in Table I). The most obvious features of these results compared with those for hydrostatic pressure is that the additional terms reduce instead of enhancing the magnitudes given by the Wong approximation $W2U = -(VT/C_P[\partial(1/E_S)/\partial T]_P$, and also that the difference between the adiabatic and mixed second derivatives is relatively much smaller than

that between the analogous pressure derivatives. This can be explained by expressing σ_U as a combination of a strong shear stress σ_{SH} and a comparatively weak negative pressure. Up to the second order, in an isotropic material these components affect the temperature independently. Although the first order shear derivative $(\partial T/\partial \sigma_{SH})_P$ is zero, the second derivatives are large and dominate the unidirectional stress derivatives. If σ_{SH} has strength equivalent to $\sigma_4 = \sigma_{SH}$, then [9]

$$(\partial^2 T/\partial \sigma_{SH}^2)_S = (-VT/C_P)\{[\partial(1/G)/\partial T]_P - \beta(1/G)\},\tag{33}$$

where $G=G_S=G_T$ is the rigidity modulus; moreover, there is no difference between the adiabatic and mixed second differentives because $(\partial T/\partial \sigma_{SH})_S=0$. The second term of eq.(33) is of opposite sign to the Wong approximation (given by the first term), reducing the magnitude. For unidirectional stress derivatives this is partially compensated by the additional terms in the small pressure contributions, which therefore lessen differences from the Wong approximation and also produce a small difference between the adiabatic and mixed derivatives. For Ti and Ti-6Al-4V corrections to W2U are particularly small, which may explain why Wong et al. [5] obtained good agreement with their experimental results for unidirectional stress despite their neglect of terms important for other types of stress.

5. CONCLUSION

We have found that errors in earlier approximations for second order thermoelastic effects in isotropic materials are substantial for compressive stress but much smaller for unidirectional stress. Elsewhere [9] we discuss (i) more complex stress fields in isotropic materials, including whether it is possible to deduce from temperature fluctuations the

separate contributions of compressive and shear stress; (ii) anisotropic materials.

ACKNOWLEDGMENT

Padmaja Akaraju thanks the Commonwealth Scholarship Commission U.K. for financial support.

References

- D. S. Mountain and J. M. B. Webber, Proc. Soc. Photo-Opt. Inst. Engrs. <u>164</u>:189 (1978).
- [2] B. A. Boley and J. H. Weiner, Theory of Thermal Stresses (Wiley, New York, 1960).
- [3] A. S. Machin, J. G. Sparrow, *Strain* <u>23</u>:27 (1987).
- [4] A. K. Wong, R. Jones and J. G. Sparrow, J. Chem. Phys. Solids <u>48</u>:749 (1987).
- [5] A. K. Wong, J. G. Sparrow and S. A. Dunn, J. Chem. Phys. Solids <u>49</u>:395 (1988).
- [6] H. Ledbetter, M. Lei and R. Ramji Rao, *Physica B* <u>159</u>:265 (1989).
- [7] Y. A. Chang, J. Chem. Phys. Solids <u>28</u>:697 (1967).
- [8] T. H. K. Barron, J. Physics: Cond. Matter <u>12</u>:L155 (1979).
- [9] T. H. K. Barron, in preparation.
- [10] T. H. K. Barron, in Thermal Expansion of Solids, C.Y.Ho, ed.(ASM International, Materials Park, Ohio, 1998), pp.1-108.
- [11] T. H. K. Barron and G. K. White, Heat Capacity and Thermal Expansion at Low Temperatures (Kluwer Academic/Plenum, New York, 1999).
- [12] A. Padmaja, Int. J. Thermophys. <u>17</u>:723 (1996).
- [13] W. A. Bassett, T. Takahashi, H.-K. Mao, and J. S. Weaver, J. Appl. Phys. <u>39</u>:319 (1968).

Table I. Experimental Data for Pressure Analysis

Material	χ_S	α	c_P	$\left(\frac{\partial \chi_S}{\partial \ln T}\right)_P$	$\left(\frac{\partial \ln \alpha}{\partial \ln T}\right)_{H}$	$\int_{\mathcal{O}} \left(\frac{\partial \ln C_P}{\partial \ln T} \right)_P$
_	TPa^{-1}	$10^{-6} \mathrm{K}^{-1}$	$J \cdot Kg^{-1} \cdot K^{-1}$	$\mathrm{TPa^{-1}}$	_	_
NaCl	39.9	39.0	864	4.70	0.257	0.145
KCl	56.1	36.3	686	5.60	0.485	0.057
Al	13.1	16.7	906	0.924	0.179	0.154
Cu	7.16	16.7	386	0.378	0.181	0.156
Ti	9.33	8.30	520	0.290	0.322	0.176
Ti6Al4V	9.43	9.14	529	0.281	0.199	0.245

Table II. Calculated Pressure Derivatives

Material	T	$\left(\frac{\partial T}{\partial P}\right)_S$	K	$\left(\frac{\partial^2 T}{\partial P^2}\right)_S$	$\left[\frac{\partial}{\partial P} \left(\frac{\partial T}{\partial P}\right)_S\right]_T$	W2P
_	K	K⋅GPa ⁻¹	TPa^{-1}	K⋅GPa ⁻²	$\text{K}{\cdot}\text{GPa}^{-2}$	K·GPa ^{−2}
NaCl	160	9.01	18.77	-1.50	-2.06	-1.15
NaCl	294	18.73	21.23	-3.30	-4.67	-2.56
NaCl	675	53.90	26.62	-11.8	-17.9	-9.22
KCl	160	12.12	25.24	-3.50	-4.53	-2.85
KCl	300	24.08	26.75	-5.46	-8.28	-4.11
KCl	550	53.03	32.14	-16.40	-23.59	-13.13
Al	160	3.52	7.32	-0.229	-0.294	-0.184
Al	300	6.12	6.80	-0.457	-0.587	-0.377
Al	550	16.68	10.11	-1.08	-1.49	-0.845
Cu	160	2.25	4.69	-0.065	-0.098	-0.050
Cu	295	4.28	4.84	-0.140	-0.205	-0.110
Cu	673	10.37	5.14	-0.368	-0.546	-0.287
Ti	223	2.34	3.49	-0.117	-0.139	-0.095
Ti	293	3.11	3.54	-0.153	-0.191	-0.124
Ti	673	8.00	3.96	-0.402	-0.507	-0.120
Ti6Al4V	295	3.46	3.91	-0.153	-0.192	-0.120

Table III. Modified Approximations for $(\partial \ln K/\partial P)_T$ at Room Temperature

Material	$\left(\frac{\partial B_S}{\partial P}\right)_T$	$\left(\frac{\partial \ln K}{\partial P}\right)_T$	$-\frac{\delta_S + 1 + \gamma}{B_S}$	$-\frac{\delta_T + 1}{B_S}$	$-\frac{(\partial B_S/\partial P)_T + 1}{B_S}$
_	-	$\mathrm{TPa^{-1}}$	$\mathrm{TPa^{-1}}$	$\mathrm{TPa^{-1}}$	$\mathrm{TPa^{-1}}$
NaCl	5.3	-249	-240	-254	-251
KCl	5.1	-344	-307	-368	-342
Al	4.9	-96	-95	-98	-78
Cu	5.5	-48	-47	-49	-47
Ti	_	-61	-60	-64	_
Ti6Al4V	_	-55	-56	-57	_

Table IV. Calculated Stress Derivatives at Room Temperature

Material	E_S^{-1}	$\left(\frac{\partial (E_S^{-1})}{\partial \ln T}\right)_P$	$\left(\frac{\partial^2 T}{\partial \sigma_{\scriptscriptstyle U}^2}\right)_S$	$\left[\frac{\partial}{\partial \sigma_{U}} \left(\frac{\partial T}{\partial \sigma_{U}}\right)_{S}\right]_{T}$	W2U
_	TPa^{-1}	TPa^{-1}	K⋅GPa ⁻²	$\text{K}\cdot\text{GPa}^{-2}$	K∙GPa ⁻²
Al	14.3	2.44	-0.923	-0.937	-0.993
Cu	7.80	0.78	-0.200	-0.208	-0.227
Ti	8.68	1.55	-0.642	-0.646	-0.662
Ti6Al4V	9.00	1.18	-0.481	-0.485	-0.505